Dynamic mechanical behavior and optical limiting property of multifunctional fullerenol/polymer composite

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Abstract

The dynamic mechanical behavior of materials based on multifunctional fullerenol and poly(styrene-co-4-vinylpyridine)/poly(styrene-co-butadiene) matrix was studied. The interaction between the hydroxyl group of fullerenol and the pyridine group as evidenced by X-ray photoelectron spectroscopy results in a significant increase of the storage modulus. The optical limiting property of fullerenol was studied at 532 nm with nanosecond laser pulses. The optical limiting performance of fullerenol, which is poorer than its parent C60, is slightly improved upon the incorporation of poly(styrene-co-4-vinylpyridine).

1. Introduction

In view of its attractive superconducting, optical, catalytic and medicinal properties, [60]fullerene (C60) has received much attention in recent years [1–8]. C60-based polymeric materials have also been an interesting topic [9–12]. A convenient way to prepare C60-based polymeric materials is simply dispersing C60 into polymeric matrices. However, the poor adhesion between C60 and polymer prevents the well dispersion of C60 in the matrix [13,14]. To enhance the affinity therein, C60 is functionalized and interacts with complementary functional groups of a polymer, and the specific interaction between C60 and the polymer plays an important role in the resulting mechanical performance and other properties [11,13–15]. However, the properties of C60 may have changed upon functionalization and after mixing with the polymer. Sun and his co-workers [16–18] have investigated the nonlinear optical properties of a series of methano-C60 derivatives, in which monofunctional C60 derivatives show similar optical limiting responses as that of parent C60 while multifunctional ones have poorer performance. Here we report an investigation on the dynamical mechanical behavior and the optical limiting properties of multifunctional fullerenol/polymer composite.
2. Experimental

2.1. Materials and sample preparation

Fullerene (C\textsubscript{60}) (99.9\%) was obtained from Peking University, China. Multifunctional fullereneol (Fol) was synthesized and characterized according to literature \[19\]. On the average, Fol has 10–12 hydroxy addends. Toluene and N,N-dimethylformamide (DMF) of AR grade were purchased from Fisher Scientific, USA and used as received. Two poly(styrene-co-4-vinylpyridine) (PSVPy) samples containing 20 and 32 mol\% of vinylpyridine, denoted as PSVPy20 and PSVPy32, respectively, were prepared by free-radical copolymerization. Poly(styrene-co-butadiene) was purchased from Aldrich, USA, which is a kind of high-impact polystyrene (HIPS) with a melt index (200 °C/5 kg, ASTM D 1238) of 2.8 g/10 min.

Fol was dissolved in DMF, into which an appropriate amount of PSVPy32 was added. The mixture was stirred continuously overnight and then added into diethyl ether dropwise with vigorous stirring. The precipitates (blends) were isolated by centrifugation and washed with diethyl ether for three times. The blends were dried in vacuo at 50 °C for 1 week. The Fol contents in various blends were determined by thermogravimetric analysis. X-ray photoelectron spectroscopic (XPS) measurements were made on these blends.

The brittleness of PSVPy made it difficult to prepare Fol/PSVPy samples for dynamic mechanical analysis (DMA) measurements. Instead, a mixture of 26 parts of PSVPy20 and 74 parts of HIPS was used as the matrix. To achieve a better compatibility between PSVPy and HIPS, PSVPy20 was used in view of its higher styrene content. Appropriate amounts of Fol, PSVPy20 and HIPS were mixed in a Laboratory Mixing Molder (ATLAS, USA) at 190 °C for 30 min at a speed of 120 rpm. The mixed samples were compacted into films with a thickness ca. 0.25 mm under a pressure of 12 MPa at 140 °C and then at room temperature at the same pressure for 30 min using a hydraulic press (Fred S. Carver, USA). The Fol contents in various samples were determined by thermogravimetric analysis. Samples used in this study are PSVPy20/HIPS polymer matrix, and polymer matrix filled with 2.4, 4.8, and 11.6 wt\% of Fol, which are denoted as Fol2.4, Fol4.8, Fol11.6, respectively.

2.2. Characterization

XPS measurements were made on a VG ESCALAB MKII spectrometer with a Mg K\textsubscript{α} X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Sample films were mounted on studs using a double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA. A pass energy of 20 eV and a rate of 0.05 eV/step were used for all XPS spectra acquisitions with a binding energy width of 12 eV. The pressure in the analysis chamber was maintained at 10\textsuperscript{−8} mbar or lower during the measurements. All spectra were obtained at a take-off angle of 75° and they were curve-fitted with XPSPEAK3.1. To compensate the surface charging effects, all binding energies were referenced to the saturated hydrocarbon C\textsubscript{1s} peak at 285.0 eV.

Dynamic mechanical behavior was investigated in film tension mode with a TA Instruments Dynamic Mechanical Analyzer (DMA 2980) under purified nitrogen at a frequency of 1 Hz and a heating rate of 3 °C min\textsuperscript{−1}. The temperature ranged from room temperature to 140 °C.

2.3. Optical limiting measurements

The concentration of Fol solution in DMF was adjusted so that its linear transmittance was 70% at 532 nm through a 1-mm optical path length (denoted as Fol-c). This Fol solution was then diluted until its linear transmittance was 70% at 532 nm through a 10-mm optical path length.
To maximize the interaction between Fol and PSVPy, PSVPy32 was used in the optical limiting study. Appropriate amount of PSVPy32 was added to both Fol-c and Fol-d, which were denoted as Fol/PSVPy32-c and Fol/PSVPy32-d, respectively. Polystyrene was similarly added to Fol-c and Fol-d and the samples were denoted as Fol/PS-c and Fol/PS-d. The introduction of polymer has a negligible effect on the linear transmittance. For comparison, two C60 solutions in toluene were similarly prepared and denoted as C60-c and C60-d, respectively.

The optical limiting responses were measured using linearly polarized 7-ns optical pulses from a Q-switched frequency-doubled Nd:YAG laser at 532 nm. The spatial distribution of the pulses was nearly Gaussian after passing through a spatial filter. The laser was operated in the single-shot mode. The pulse was divided by a beam splitter into two parts. The reflected part was taken as the reference representing the incident light energy and the transmitted beam was focused by a 25-cm focal length lens through the sample. Both the incident and transmitted pulse energies were measured simultaneously by two energy detectors (Laser Precision RJP-735). The minimum beam waist of the focused laser beam was 35 \( \mu \)m, measured by the standard Z-scan method [20]. The optical limiting measurements were conducted with the sample fixed at the focus. In order to maintain the linear transmittance of sample solutions at 70%, quartz cuvettes with different optical path lengths were used, i.e., 10 mm-thick cuvettes for dilute solutions and 1 mm-thick cuvettes for concentrated solutions.

### 3. Results and discussion

#### 3.1. Interaction between Fol and PSVPy

An important factor which affects the properties of polymer composites is the interfacial adhesion between matrix and filler. We have previously found that interactions between C60 derivatives and complementary functional groups of polymers ensure a good interfacial adhesion and result in a better reinforcing effect [14,15]. The interaction between the hydroxyl group of Fol and the pyridine nitrogen of PSVPy32 is evident from XPS studies (Fig. 1). The N1s spectrum of PSVPy32 shows a symmetrical peak centered at 399.3 eV. In contrast, the N1s peak of a Fol/PSVPy32 blend containing 41.4 wt% of Fol is broader and asymmetrical. The N1s peak of the blend can be curve-fitted by two component peaks, with one remaining at 399.3 eV and the other at 400.1 eV. The development of a new high binding energy peak clearly shows that some of the pyridine nitrogen atoms interact with Fol. Since the binding energy is increased by 0.8 eV, the interaction between Fol and PSVPy32 is hydrogen-bonding interaction. An ionic interaction will lead to an increase in binding energy by 2.0 eV or more [21–23].

#### 3.2. Dynamic mechanical behavior

As shown in Fig. 2, all filled samples have much higher storage moduli than that of unfilled poly-
meric matrix in the glassy state. The storage modulus increases with increasing Fol content, with Fol11.6 having a storage modulus nearly double than that of unfilled polymeric matrix. The reinforcing effects of C₆₀ and its derivatives in polymer composites have already been observed [14,15]. It is noted that the reinforcing effect of Fol diminishes at higher temperatures and all materials have nearly the same moduli beyond 100 °C. We have found that the reinforcing effect of a monofunctional carboxylic acid derivative of C₆₀ on PSVPy/HIPS matrix also diminishes in the glass-rubber transition region [14]. However, we have recently found that the reinforcing effect of a multifunctional $N$-(2-aminoethyl)aminofullerene (AEAF) is sustained in the glass-rubber transition region of poly(ethylene-co-acrylic acid) containing 20 wt% of acrylic acid (PEAA20) [15]. We suggested that the multifunctional nature of AEAF produced a network-like material and thus the reinforcing effect of AEAF could be sustained at high temperatures. The inability of Fol to sustain its reinforcing effect at high temperatures may be attributed to the following factors. First, the matrix is a mixture of PSVPy20 and HIPS, and hence

Fig. 3. $\tan \delta$ plots for various samples. See Fig. 2 for sample codes.

Fig. 4. The ground state absorption spectra of various samples. (a) C₆₀-d and Fol-d before laser irradiation. (b) C₆₀-d and Fol-d after laser irradiation. (c) C₆₀-c and Fol-c before (solid line) and after laser irradiation (dash line) (d) Curve 1-Fol-c, curve 2-Fol/PS-c, and curve 3-Fol/PSVPy32-c₂ after laser irradiation.
the content of the interacting site, the vinylpyridine unit, is low (around 4.6 mol% pyridine unit as determined by elemental analysis). In comparison, the PEAA20 matrix is not diluted by other polymers. Secondly, Fol interacts with PSVPy through hydrogen-bonding interaction whereas AEAF interacts with PEAA20 through ionic interaction. As a result, the overall interaction between Fol and PSVPy20 is not as strong as that between AEAF and PEAA20, and therefore the reinforcing effect of Fol in the PSVPy20/HIPS is not sustained at high temperatures.

Fig. 3 shows the tan δ peaks of various composites. The incorporation of Fol has no significant effect on the tan δ peak. The incorporation of monofunctional carboxylic acid derivative of C60 also produces no significant effect on the tan δ peak of the PSVPy/HIPS matrix [14]. On the other hand, the tan δ peak of PEAA20 slightly broadens and moves to a higher temperature upon the incorporation of multifunctional AEAF [15]. The stronger interaction between AEAF and PEAA20 makes the polymer chain less mobile and thus the tan δ peak moves to a higher temperature.

3.3. Optical limiting property

Fig. 4 shows the ground-state absorption spectra of various samples before and after laser irradiation, and the parameters are summarized in Table 1. The spectrum of Fol is structureless in the visible region, which is different from that of C60. The molar absorptivity (ε) of Fol is 1080 M⁻¹ cm⁻¹, much higher than that of 50 M⁻¹ cm⁻¹ for the hexakis-adducts of methano-C60 derivative [17]. The addition of polymers has negligible effects on the absorption spectrum and the molar absorptivity of Fol. C60 and Fol possess good photostability as shown by their practically identical UV–Vis spectra before and after laser irradiation. The addition of polymers does not affect the photostability of Fol. Tables 1 and 2 list the solutions for optical limiting measurements, where polymer-containing Fol solutions were prepared by adding appropriate amounts of polystyrene and PSVPy32 into Fol-d and Fol-c solutions. DMF solutions of polystyrene and PSVPy32 with similar concentrations as the Fol/PSVPy32-c2 solution were also measured to examine possible optical limiting contribution. Fig. 5 shows the optical limiting responses of

<table>
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<tr>
<th>Sample code</th>
<th>Fullerene concentration (M)</th>
<th>Polymer concentration (mg/ml)</th>
<th>Pyridine/Hydroxyl molar ratio</th>
</tr>
</thead>
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<tr>
<td>Fol/PS-c</td>
<td>1.42 × 10⁻⁴</td>
<td>1.0</td>
<td>–</td>
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<tr>
<td>Fol/PS-d</td>
<td>1.42 × 10⁻⁴</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
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<td>1.0</td>
<td>1/5</td>
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<tr>
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<td>1.42 × 10⁻³</td>
<td>5.3</td>
<td>1/1</td>
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<tr>
<td>Fol/PSVPy32-d1</td>
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<td>0.5</td>
<td>1/1</td>
</tr>
<tr>
<td>Fol/PSVPy32-d2</td>
<td>1.42 × 10⁻⁴</td>
<td>1.0</td>
<td>2/1</td>
</tr>
<tr>
<td>Polystyrene</td>
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<td>5.1</td>
<td>–</td>
</tr>
<tr>
<td>PSVPy32</td>
<td>–</td>
<td>5.4</td>
<td>–</td>
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</table>
various samples. The input fluences for C$_{60}$ solutions were limited below 6 J/cm$^2$ because they exhibit optical damage at a higher input fluence. As shown in Fig. 5a, the optical limiting responses of both C$_{60}$ and Fol are concentration dependent, where a concentrated solution has a better performance than a dilute one. Moreover, Fol has a weaker optical limiting response than C$_{60}$ does. Both polystyrene and PSVPy32 have no optical limiting responses (Fig. 5b). Figs. 5c, d show the effect of polymers on the optical limiting performance of Fol. The addition of polystyrene does not significantly affect the optical limiting performance of Fol regardless of concentration of Fol (Fig. 5c). PSVPy32 shows similar effects as polystyrene on the optical limiting performance of dilute Fol solution. However, PSVPy32 slightly improves the performance of concentrated Fol solution at a higher pyridine/hydroxyl ratio. Riggs and Sun [16,17] investigated the effect of solution viscosity on the optical limiting performance of a series of methano-C$_{60}$ derivatives. They found that monofunctional methano-C$_{60}$ derivatives have similar optical limiting response to C$_{60}$, while multifunctional methano-C$_{60}$ derivatives show poorer response. Moreover, the optical limiting responses of fullerene solutions are concentration dependent, with concentrated solution having better performance than dilute one. It was also revealed that the high viscosity of solution due to the addition of high molecular weight poly(methyl methacrylate) or poly(propionylethyleneimine) would reduce the optical limiting performance of methano-C$_{60}$ derivatives. They attributed both the solution concentration dependence and medium viscosity dependence of optical limiting properties to be associated with excited triplet-state bimolecular processes in reverse saturable absorption mechanism. In the present study,

![Graphs showing optical limiting responses of various samples.](image)

Fig. 5. Optical limiting responses of various samples in a constant 70% linear transmittance at 532 nm. (a) Toluene solutions of C$_{60}$-c (●), C$_{60}$-d (○), and DMF solutions of Fol-c (▲), Fol-d (△). (b) DMF solutions of PS (□), PSVPy32 (■). (c) DMF solutions of Fol-c (▲), Fol/PS-c (+), Fol-d (△), Fol/PS-d (+). (d) DMF solutions of Fol-c (▲), Fol/PSVPy32-c$_1$ (○), Fol/PSVPy32-c$_2$ (□), and Fol-d (△), Fol/PSVPy32-d$_1$ (■), Fol/PSVPy32-d$_2$ (×).
since the polymer concentration is low (0.5–5.4 mg/ml), the solution viscosity is very low as compared to the case of Riggs and Sun (250–400 mg/ml). Therefore, the reduction of optical limiting performance is not obvious after the addition of polystyrene or PSVPy32 to dilute Fol solution. On the other hand, the slight improvement of the optical limiting performance upon the incorporation of PSVPy32 into concentrated Fol solution might be caused by the strong interactions between PSVPy32 and Fol.

4. Conclusion

XPS spectra show the existence of hydrogen-bonding interaction between the hydroxyl group of Fol and the pyridine nitrogen atom of PSVPy. Compared to unfilled polymeric matrix, Fol/polymer composite has a much higher storage modulus, which increases with increasing Fol content. Compared to C60, Fol shows a weaker nonlinear optical response, which may be ascribed to the disturbance of π-electronic system of parent C60 molecule due to multifunctionalization. Polystyrene does not significantly change the optical limiting performance of Fol solution, while PSVPy32 slightly improves the optical limiting performance of concentrated Fol solution.

Acknowledgements

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References